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A new class of closed-cell aluminium foams reinforced with carbon nanotubes

I. Duarte[a,*], E. Ventura[a], S. Olhero[b], J.M.F. Ferreira[b]

[a]*Department of Mechanical Engineering, TEMA, University of Aveiro, Campus Universitário de Santiago, 3810–193 Aveiro, Portugal*
[b]*Department of Materials and Ceramics Engineering, CICECO, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal*

Abstract

This manuscript reports on the fabrication of closed-cell aluminium alloy foams reinforced with carbon nanotubes (CNTs) through a novel approach that combines the powder metallurgy method with colloidal processing step that grants uniform dispersion of CNTs into the aqueous suspension of all powder components. Spraying the as prepared suspension into liquid nitrogen followed by lyophilisation enables obtaining homogeneous spherical granules to be used in the powder metallurgy method. Besides ensuring good dispersion of all powder components in the system, the non-agglomerated form of CNTs and the expansion upon foaming foster their structural integrity under stretched conditions in the final foams for an efficient load transfer.
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Keywords: reinforced aluminium foams; carbon nanotubes; freeze-granulation; powder metallurgy.

1. Introduction

Lightweight, recyclable, non-flammable closed-cell metal foams with excellent energy absorption capacity to impact and good sound damping are being used in commercial and military applications [1]. Despite the wide variety of foams, in which some processes allow very good control of the density [2] and cellular structure [3], its mechanical strength is limited. Due to this limitation, such materials are rarely used alone. In general, these foams are rather incorporated into composite structures. For example, as core materials into sandwich panels [4], as stiffeners into shell structures for inhibiting buckling, as energy absorbing members into structural energy-absorbing parts in zones of vehicles more subjected to collapse (crash structures) to absorb and dissipate energy [5-7]. One of the main current challenges of scientific community in this field is to increase the mechanical strength of such materials to prepare high strength metallic foams. Some studies have been conducted to achieve this goal through the incorporation of reinforcements (e.g. ceramic particles) [8], or by promoting the formation of the intermetallics [9-10]. For example, the addition of the Sc [9] and Mn [10] alloying elements could increase the yield strength of the Al-alloy foam due to the formation of Al_6Mn and Al_3Sc. Despite some works reporting that ceramic particles improve the mechanical properties of open-cell metal foams, the opposite happens for closed-cell metal foams [11]. It is well-known that ceramic particles are responsible to the brittle behaviour of closed-cell metal foams prepared using direct foaming methods that use these particles to control the viscosity of the metal melt [1,3]. Attempting to answer to this more demanding challenge, a new class of closed-cell metal foams, also designates as nanocomposite metal foams, was developed by combining the remarkable

* Corresponding author.
E-mail address: isabel.duarte@ua.pt (I. Duarte)

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properties of metal matrices and CNTs. As well-known, carbon nanotubes are being considered as an ideal material to reinforce ceramic, polymer and metal matrices for improving their mechanical thermal and electrical properties [11-13]. While the reinforcement of polymeric matrices with CNTs is reasonably well established, its incorporation into metals is still a challenge. This is due to the high tendency of CNTs to agglomerate into clusters, their poor dispersion ability in the metal-matrix, and the poor wettability of carbon by molten metals due to a large difference of surface tensions. The eventual formation of interfacial reaction product leading to loss of structural integrity is added difficulty. To overcome such problems, several manufacturing process have been developed [13], among which the powder metallurgy (PM) method is the most extensively studied. The PM process is also one of the most versatile methods to fabricate closed-cell foams [14-15]. Based on it, an innovative method combining powder technology and colloidal processing (based on freeze-granulation, followed lyophilisation) was recently established by the authors to fabricate Al-alloy foams reinforced with CNTs, also called closed-cell nanocomposite foams.

2. Experimental

Aluminium alloy powder (as metal; average diameter: 32 µm), titanium hydride powder (0.6 wt.%, as blowing agent; average diameter: 6.9 µm) and multi-wall carbon nanotubes (0.5 wt.%, as reinforcement; outer diameter: <8 nm; inner diameter: 2–5 nm; length: 10–30 mm; content of COOH: 3.67–4.05 %) were used as main starting materials in this work. Dolapix CE64, conventional detergent and Nanosperse AQ (0.96 wt.%, a commercial dispersant for MWCNTs supplied by NanoLab Inc), Polyvinyl alcohol (1.5 wt.%) was also tested as dispersant, binder and surfactant. A freeze granulator (LS-2 model, PowderPro AB), a liophilizer (Testlar), an in-house assembled hot press (maximum load: 20 ton) and a batch furnace (maximum temperature: 1000 ºC) were the main facilities used in this work to fabricate the closed-cell aluminium foams reinforced with MWCNTs. The spherical granules were prepared by spraying an aqueous suspension containing all the solids components (Al-alloy, TiH_2 and MWCNTs) through a nozzle of 1.2 mm into liquid nitrogen using peristaltic pump at 30 rpm under pressurized air of 0.8 bar. The liquid droplets were quickly frozen forming spherical granules, which were then lyophilized at −80ºC under 0.022 mbar. The spherical granules were consolidated by uniaxial hot pressing at 400ºC under an applied pressure of 278 MPa. Foaming was conducted in a furnace preheated at 700ºC.

3. Results and Discussion

We proposed a novel approach with the addition of a colloidal processing step (Fig. 1) to the traditional PM method for dispersing and incorporating the MWCNTs into the aluminium and titanium hydride powders. Thus, the new proposed method is divided into three main steps instead the traditional two manufacturing steps, as shown in Fig. 2 [16]: (i) the preparation of the granules by freeze granulation (FG); (ii) the preparation of the foamable precursor and (iii) the preparation of the reinforced foams. For the preparation of spherical granules by freeze-granulation in the first step, a stable and highly solids loaded aqueous suspension was previously prepared with proper rheological behaviour for flowing through the spraying nozzle (Fig. 1).

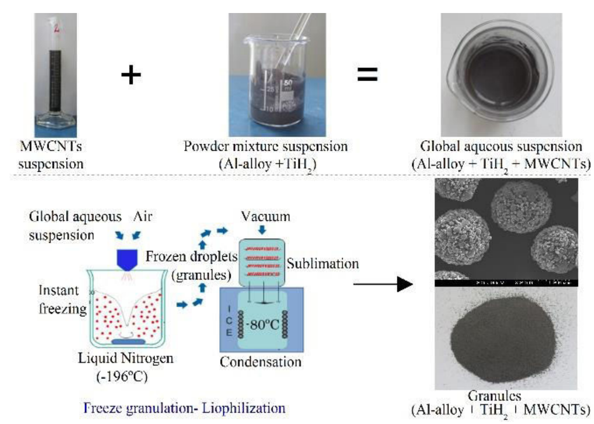

Fig. 1. New colloidal processing step add to the powder metallurgy method. Highly-spherical granules prepared by FG-Lyophilisation.

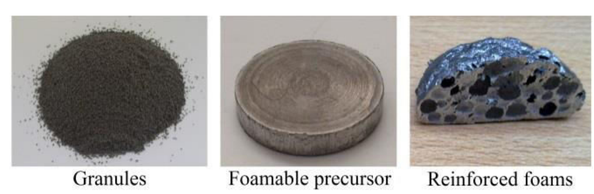

Fig. 2. Different products prepared during the new approach method.

The main difference between the conventional PM method and the new approach is that the precursor is prepared using spherical granules (Figs. 1 and 2) instead from the conventional powder mixture [14-15]. The results demonstrated that the FG technique is proper to preserve in the granules the high degree of homogeneity achieved in the starting suspension containing of all components (Al-alloy, TiH_2 and functionalized MWCNTS), Fig. 2. A conceptual paper on the preparation of spherical granules by FG and their compaction to obtain the precursor materials, including some preliminary results, was firstly reported [16].

Evidences about the good dispersion of MWCNTs inside the precursor materials (Fig. 2) were shown. In a following paper [17], the influences of some of the most relevant processing variables were investigated aiming at establishing the optimal conditions along the different manufacturing steps. A systematic study on the dispersion behaviour of MWCNTs was conducted using different dispersing agents, while evaluating their synergetic dispersing actions were assessed through complementary techniques (sedimentation and zeta potential measurements using diluted suspensions). Concentrated suspensions prepared under selected conditions were also used for rheological measurements. Fig. 3 shows detailed microstructural evidences observed by SEM about the uniform dispersion of MWCNTs and TiH_2 in the Al-alloy matrix along the entire process. The MWCNTs appeared directionally aligned in the Al-alloy matrix of the foams, indicating that their tubular structure was retained throughout the whole process.

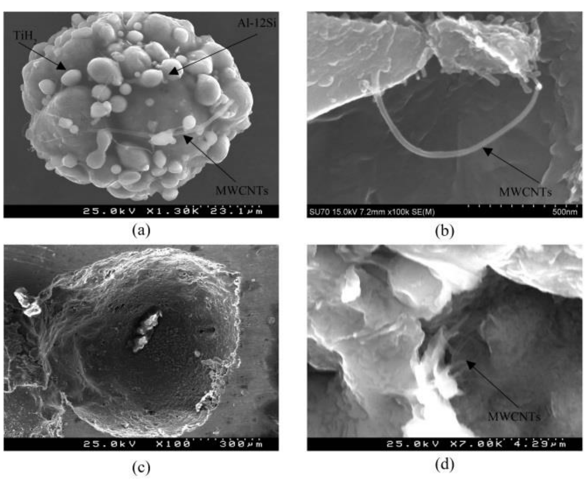

Fig. 3. (a) Surface of a granule with 0.5 wt.% MWCNTs-COOH showing their good dispersion in the Al-alloy and TiH_2 powders; (b) Surface of the corresponding precursor exhibiting a MWCNTs-COOH. (c) Cellular pore and (d) Pore cell-wall with MWCNTs.

The SEM images of the completely fractured composite surface showed clear evidences of ruptured MWCNTs. The observed microstructural features of both MWCNTs-containing precursor material and closed-cell foams provide clear evidences that carbon nanotubes are individually dispersed, stretched and randomly aligned in the aluminium-matrix. The tubular structure of MWCNTs was retained throughout the whole process. These are key requirements to potentiate the homogeneous 3D reinforcing role of MWCNTs and to provide an efficient load transfer. As a result, great increases in Vickers micro-hardness were achieved for the nano-composite Al-foams. The results confirmed that Al-foams reinforced with 0.5 wt.% MWCNTs exhibit average values that are >55 % in comparison to the non-reinforced ones, although increments >100% were registered in some cases, depending on the neighbourhood between of the indentation point and the reinforcing MWCNTs. The Vickers microhardness measured for non-reinforced foams were 60 HV ± 5.18 HV, while those of reinforced ones were significantly higher (93.43 HV± 19.30 HV), reaching a maximum value of 135 HV.

These results constitute a proof of the concept and represent significant advances in the state of the art. As a matter of fact, in the generality of the previous literature reports on metallic matrix composites reinforced with carbon nanotubes, CNTs tend to appear in clusters, therefore, annulling their reinforcing potential.

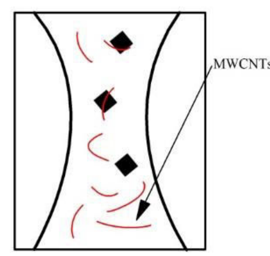

Fig 4. Schematic illustration of cell wall showing the dispersion of MWCNTs.

The understanding how the carbon nanotubes act to reinforce a composite is vital. This issue has been tackled recently by Chen et al. [18]. The researchers used a powder metallurgy route to fabricate an Al metal matrix composite reinforced with 0.6 wt. % MWCNTs produced by chemical vapour deposition and performed *in-situ* tensile tests on MWCNT-reinforced Al-matrix composites. This advanced *in-situ* tensile measurements were performed by operating the tensile stage with a CNTs/Al sample inside a FE-SEM chamber. The authors stated that this *in-situ* SEM observation technique provides a direct and easy method to investigate the mechanical behaviour of MWCNTs in composites, which is essentially regulated through a load transfer strengthening mechanism. When a force is applied to the composite, the MWCNTs initially act like a bridge to suppress crack growth. As further force is applied, the outer walls of the nanotubes in contact with the Al matrix start to break. The inner walls then fracture, either breaking vertically or unpeeling to expose the next inner walls, and so on. Chen et al. [18] have also reviewed and discussed the several possible strengthening mechanisms already proposed for CNTs in metal-matrix composites. Several strengthening mechanisms have been already proposed for MWCNTs in metal-matrix composites (MMCs) [18-23], including load transfer from matrix to MWCNTs [18], dispersion strengthening of MWCNTs [19], solution strengthening of carbon atoms [20], strengthening of in-situ formed carbide particles [21], grain refining [22] and texture strengthening by pinning effect of MWCNTs [23], and thermal mismatch between MWCNTs and matrix. But, the composite strength might be a synergetic result of several strengthening mechanisms although the specific contribute of each one is not easy to discriminate from these previous reports [18-23].

4. Conclusions

The main challenge towards developing an innovative process to fabricate Al-foams reinforced with MWCNTs (called nanocomposites foams) was successfully overcome. The novel approach to fabricate foams reinforced with MWCNTs (called foams nanocomposites) ensures a homogeneous dispersion of CNTs throughout the metal matrix and the retention of chemical and structural stability of CNTs to be achieved. These key requirements potentiate the homogeneous 3D reinforcing role of MWCNTs and to provide an efficient load transfer. The non-fulfilment of these conditions explain why the generality of the previous attempts reported in literature were not successful as carbon nanotubes tend to appear in clusters in the metallic matrix, therefore, annulling their reinforcing potential. Increments in Vickers microhardness of Al-foams reinforced with just 0.5 wt.% varied within the range of 55-125% in comparison to the non-reinforced ones. This variability depends solely on the neighbourhood between the indentation point and the reinforcing MWCNTs, as we gave enough evidences about the excellent dispersion of the CNTs in the Al matrix. Such an achievement was possible taking into account the benefits of freeze-granulation which is a technique used in colloidal processing of ceramic and composite materials.

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References

[1] H.-P. Degischer, B. Kriszt. Handbook of Cellular Metals: Production, Processing, Applications, Wiley-VCH Verlag GmbH & Co. KgaA, 2002.
[2] I. Duarte, J. Banhart. Acta Mater. 48 (2000) 2349.
[3] J. Banhart. Adv. Eng. Mater. 15 (2013) 82.
[4] J. Banhart, H. W. Seeliger. Adv. Eng. Mater. 10 (2008) 793.
[5] I. Duarte, M. Vesenjak, L. Krstulović-Opara, I. Anžel, J.M.F. Ferreira, Mater. Design 66 (2015) 532.
[6] I. Duarte, M. Vesenjak, L. Krstulović-Opara, Z. Ren, Compos. Struct. 124 (2015) 128.
[7] I. Duarte, M. Vesenjak, L. Krstulović-Opara, Compos. Struct. 109 (2014) 48.
[8] M. Alizadeh, M. Mirzaei-Aliabadi, Mater. Design 35 (2012) 419.
[9] L. Huang, H. Wang, D.H. Yang, F. Ye, Z.P. Lu, Intermetallics 28 (2012) 71.
[10] X. Xia, H. Feng, X. Zhang, W. Zhao. Mater. Design 51 (2013) 797.
[11] I. Duarte, J.M.F. Ferreira. Materials 9 (2016) 79.
[12] P.J.F. Harris. Carbon nanotube science: synthesis, properties and applications, Cambridge University Press, 2nd edition, Cambridge, 2011.
[13] C. Tjong, Mater. Sci. Eng. R 74 (2013) 281.
[14] F Baumgärtner, I Duarte, J Banhart, Adv. Eng. Mater. 2 (2000) 168.
[15] I. Duarte, M. Oliveira, in: K. Kondoh (Ed.), Powder Metallurgy. InTech. 2012. pp. 47–72.
[16] I. Duarte, E. Ventura, S. Olhero, J.M.F. Ferreira, Mater. Letters 160 (2015) 162.
[17] I. Duarte, E. Ventura, S. Olhero, J.M.F. Ferreira, Carbon 95 (2015) 589.
[18] B. Chen, S. Li, H. Imai, L. Jia, J. Umeda, M. Takahashi, K. Kondoh, Compos. Sci. Technol. 113 (2015) 1.
[19] R. George, K.T. Kashyap, R. Rahul, S. Yamdagni, Scr. Mater. 53 (2005) 1159.
[20] S.J. Yoo, S.H. Han, W.J. Kim, Scr. Mater. 68 (2013) 711.
[21] S. Li, B. Sun, H. Imai, K. Kondoh, Carbon 61 (2013) 216.
[22] D.H. Nam, S.I. Cha, B.K. Lim, H.M. Park, D.S. Han, S.H. Hong, Carbon 50 (2012) 2417.
[23] H. Wei, Z. Li, D.-B. Xiong, Z. Tan, G. Fan, Z. Qin, D. Zhang, Scr. Mater. 75 (2014) 30.